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<p>(54) Title: FLAME RETARDANT POLYCARBONATE/RUBBER-MODIFIED GRAFT COPOLYMER RESIN BLENDS HAVING A LOW FLUORINE CONTENT</p> <p>(57) Abstract</p> <p>A thermoplastic resin composition that contains an aromatic polycarbonate resin, a rubber modified graft copolymer comprising a discontinuous elastomeric phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase, a phosphorus containing flame retardant compound, and a fluoropolymer, in an amount effective to improve the flame retardant performance of the composition, provided that the fluorine content of the composition does not exceed 0.1 percent by weight fluorine.</p>			

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## FLAME RETARDANT POLYCARBONATE/RUBBER-MODIFIED GRAFT COPOLYMER RESIN BLENDS HAVING A LOW FLUORINE CONTENT

## FIELD OF THE INVENTION

The invention relates to flame retardant resin compositions that are based on blends of polycarbonate resin and rubber modified graft copolymers and that have a low halogen content.

## BRIEF DESCRIPTION OF THE RELATED ART

Flame retardant compositions containing an aromatic polycarbonate resin a graft copolymer, a fluoropolymer and a phosphorus containing flame retardant compound are known and have been found to exhibit good flame retardency and good heat resistance, see for example, coassigned U.S. Patent Number 5,204,394. The compositions in the '394 patent contain, for example, from 0.2 to 0.5 parts by weight (pbw) per 100 parts by weight

5 polytetrafluoroethylene per 100 pbw of the composition. In some applications, the amount of fluorine that may be contained in a composition is limited by government regulations, such as, for example, DIN/VDE 0472, Part 815, Test B, which limits allowable fluorine content to less than or equal to 0.1 percent by weight fluorine.

10

15 A thermoplastic resin composition that exhibits the high performance and good flame retardant properties of the compositions disclosed in the '394 patent and that exhibit a low fluorine content are desired.

## SUMMARY OF THE INVENTION

The thermoplastic resin composition of the present invention comprises:

20 (a) an aromatic polycarbonate resin,

- (b) a rubber modified graft copolymer comprising a discontinuous elastomeric phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase,
- 5 (c) a phosphorus containing flame retardant compound, and
- (d) a fluoropolymer, in an amount effective improve the flame retardant performance of the composition, provided that the fluorine content of the composition does not exceed 0.1 percent by weight fluorine.

10 The composition of the present invention meets the low fluorine content requirements of DIN/VDE 0472 Part 815, Test B yet unexpectedly provides high performance and good flame retardant properties.

#### DETAILED DESCRIPTION OF THE INVENTION

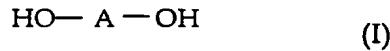
In a preferred embodiment, the thermoplastic resin composition of the present invention is comprises, based on 100 pbw of the composition, from 60 to 95 pbw, more preferably from 75 to 95 pbw, even more preferably from 80 to 90 pbw, of the polycarbonate resin, from 1 to 15 pbw, more preferably from 4 to 10 pbw, even more preferably from 5 to 7 pbw, of the rubber modified graft copolymer, from 3 to 15 pbw, more preferably from 5 to 12 pbw, even more preferably from 8 to 10 pbw, of the phosphorus containing flame retardant compound, and wherein the amount of fluoropolymer is effective to provide a fluorine content of from 0.038 to 0.1 pbw, more preferably from 0.05 to 0.1 pbw, even more preferably from 0.08 to 0.1 pbw, fluorine.

#### Aromatic Polycarbonate Resin

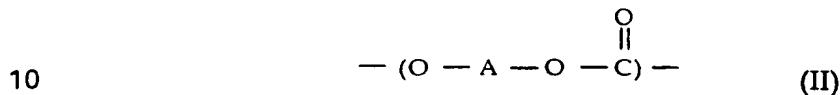
Aromatic polycarbonate resins suitable for use as the polycarbonate resin component of the thermoplastic resin composition of the present invention are known compounds whose preparation and properties have been described, see, generally, U.S. Patent Nos. 3,169,121, 4,487,896 and

5,411,999, the respective disclosures of which are each incorporated herein by reference.

In a preferred embodiment, the aromatic polycarbonate resin component of the present invention is the reaction product of a dihydric phenol according to the structural formula (I):



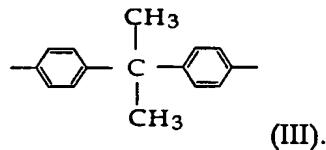
wherein A is a divalent aromatic radical, with a carbonate precursor and contains structural units according to the formula (II):



wherein A is defined as above.

As used herein, the term "divalent aromatic radical" includes those divalent radicals containing a single aromatic ring such as phenylene, those divalent radicals containing a condensed aromatic ring system such as, for example, naphthlene, those divalent radicals containing two or more aromatic rings joined by a non-aromatic linkage, such as for example, an alkylene, alkylidene or sulfonyl group, any of which may be substituted at one or more sites on the aromatic ring with, for example, a halo group or (C<sub>1</sub>-C<sub>6</sub>)alkyl group.

20 In a preferred embodiment, A is a divalent aromatic radical according to the formula (XXI):



Suitable dihydric phenols include, for example, one or more of 2, 2-bis(4-hydroxyphenyl) propane ("bisphenol A"), 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, bis(4-hydroxyphenyl) methane, 4,4-bis(4-

hydroxyphenyl)heptane, 3,5,3',5'-tetrachloro-4,4'-dihydroxyphenyl)propane, 2,6-dihydroxy naphthalene, hydroquinone, 2,4'-dihydroxyphenyl sulfone. In a highly preferred embodiment, the dihydric phenol is bisphenol A.

The carbonate precursor is one or more of a carbonyl halide, a 5 carbonate ester or a haloformate. Suitable carbonyl halides include, for example, carbonyl bromide and carbonyl chloride. Suitable carbonate esters include, such as for example, diphenyl carbonate, dichlorophenyl carbonate, dinaphthyl carbonate, phenyl tolyl carbonate and ditolyl carbonate. Suitable haloformates include, for example, bishaloformates of a dihydric phenols, 10 such as, for example, hydroquinone, or glycols, such as, for example, ethylene glycol, neopentyl glycol. In a highly preferred embodiment, the carbonate precursor is carbonyl chloride.

Suitable aromatic polycarbonate resins include linear aromatic polycarbonate resins and branched aromatic polycarbonate resins. Suitable 15 linear aromatic polycarbonates resins include, e.g., bisphenol A polycarbonate resin. Suitable branched polycarbonates are known and are made by reacting a polyfunctional aromatic compound with a dihydric phenol and a carbonate precursor to form a branched polymer, see generally, U. S. Patent Nos. 3,544,514, 3,635,895 and 4,001,184, the respective disclosures of which are 20 incorporated herein by reference. The polyfunctional compounds are generally aromatic and contain at least three functional groups which are carboxyl, carboxylic anhydrides, phenols, haloformates or mixtures thereof, such as, for example, 1,1,1-tri(4-hydroxyphenyl)ethane, 1,3,5,-trihydroxybenzene, trimellitic anhydride, trimellitic acid, trimellityl trichloride, 4- 25 chloroformyl phthalic anhydride, pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, benzophenonetetracarboxylic acid, benzophenone-tetracarboxylic dianhydride. The preferred polyfunctional aromatic compounds are 1,1,1-tri(4-hydroxyphenyl)ethane, trimellitic anhydride or trimellitic acid or their haloformate derivatives.

In a preferred embodiment, the polycarbonate resin component of the present invention is a linear polycarbonate resin derived from bisphenol A and phosgene.

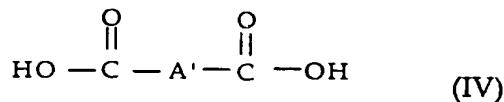
In a preferred embodiment, the weight average molecular weight of 5 the polycarbonate resin is from about 10,000 to about 200,000 grams per mole ("g/mol"), as determined by gel permeation chromatography relative to polystyrene. Such resins typically exhibit an intrinsic viscosity of about 0.3 to about 1.5 deciliters per gram in methylene chloride at 25°C.

Polycarbonate resins are made by known methods, such as, for 10 example, interfacial polymerization, transesterification, solution polymerization or melt polymerization.

Copolyester-carbonate resins are also suitable for use as the aromatic polycarbonate resin component of the present invention. Copolyester-carbonate resins suitable for use as the aromatic polycarbonate resin 15 component of the thermoplastic resin composition of the present invention are known compounds whose preparation and properties have been described, see, generally, U.S. Patent Nos. 3,169,121, 4,430,484 and 4,487,896, the respective disclosures of which are each incorporated herein by reference.

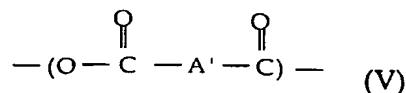
Copolyester-carbonate resins comprise linear or randomly branched 20 polymers that contain recurring carbonate groups, carboxylate groups and aromatic carbocyclic groups in the polymer chain, in which at least some of the carbonate groups are bonded directly to the ring carbon atoms of the aromatic carbocyclic groups.

In a preferred embodiment, the copolyester-carbonate resin component 25 of the present invention is derived from a carbonate precursor, at least one dihydric phenol and at least one dicarboxylic acid or dicarboxylic acid equivalent. In a preferred embodiment, the dicarboxylic acid is one according to the formula (IV):



wherein A' is alkylene, alkylidene, cycloaliphatic or aromatic and is preferably a non-substituted phenylene radical or a substituted phenylene radical that is substituted at one or more sites on the aromatic ring, wherein

5 each of such substituent groups is independently (C<sub>1</sub>-C<sub>6</sub>) alkyl, and the copolyester carbonate resin comprises first structural units according to formula (II) above and second structural units according to formula (V):



wherein A' is defined as above.

10 Suitable carbonate precursors and dihydric phenols are those disclosed above.

Suitable dicarboxylic acids, include, for example, phthalic acid, isophthalic acid, terephthalic acid, dimethyl terephthalic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dimethyl malonic acid, 1,12-dodecanoic acid, *cis*-1,4-cyclohexane dicarboxylic acid, *trans*-1,4-cyclohexane dicarboxylic acid, 4,4'-bisbenzoic acid, naphthalene-2,6-dicarboxylic acid. Suitable dicarboxylic acid equivalents include, for example, anhydride, ester or halide derivatives of the above disclosed dicarboxylic acids, such as, for example, phthalic anhydride, dimethyl terephthalate, succinyl chloride.

In a preferred embodiment, the dicarboxylic acid is an aromatic dicarboxylic acid, more preferably one or more of terephthalic acid and isophthalic acid.

In a preferred embodiment, the ratio of ester bonds to carbonate bonds present in the copolyester carbonate resin is from 0.25 to 0.9 ester bonds per carbonate bond.

In a preferred embodiment, the copolyester-carbonate copolymer has a weight average molecular weight of from about 10,000 to about 200,000 g/mol.

Copolyester-carbonate resins are made by known methods, such as, for 5 example, interfacial polymerization, transesterification, solution polymerization or melt polymerization.

#### Rubber Modified Thermoplastic Resin

Rubber modified thermoplastic resins suitable as the rubber modified thermoplastic resin of the present invention comprise a discontinuous 10 elastomeric phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase.

##### (a) Elastomeric Phase

Suitable materials for use as the elastomeric phase are polymers those 15 having a glass transition temperature ( $T_g$ ) of less than or equal to 25°C, more preferably less than or equal to 0 °C, and even more preferably less than or equal to -30°C. As referred to herein, the  $T_g$  of a polymer is the  $T_g$  value of polymer as measured by differential scanning calorimetry (heating rate 20° C/minute, with the  $T_g$  value being determined at the inflection point).

20 In a preferred embodiment, the elastomer phase comprises a polymer having repeating units derived from one or more monoethylenically unsaturated monomers selected from conjugated diene monomers, non-conjugated diene monomers or (C<sub>1</sub>-C<sub>12</sub>) alkyl (meth)acrylate monomers

25 Suitable conjugated diene monomers include, e.g., 1,3-butadiene, isoprene, 1,3-heptadiene, methyl-1,3-pentadiene, 2,3-dimethylbutadiene, 2-ethyl-1,3-pentadiene, 1,3-hexadiene, 2, 4, hexadiene, dichlorobutadiene, bromobutadiene and dibromobutadiene as well as mixtures of conjugated

diene monomers. In a preferred embodiment, the conjugated diene monomer is 1,3-butadiene.

Suitable non-conjugated diene monomers include, e.g., ethylidene norbornene, dicyclopentadiene, hexadiene or phenyl norbornene.

5 As used herein, the term "(C<sub>1</sub>-C<sub>12</sub>)alkyl" means a straight or branched alkyl substituent group having from 1 to 12 carbon atoms per group and includes, e.g., methyl, ethyl, n-butyl, sec-butyl, t-butyl, n-propyl, iso-propyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl and dodecyl, and the terminology "(meth)acrylate monomers" refers collectively to acrylate 10 monomers and methacrylate monomers. Suitable (C<sub>1</sub>-C<sub>12</sub>)alkyl (meth)acrylate monomers include (C<sub>1</sub>-C<sub>12</sub>)alkyl acrylate monomers, e.g., ethyl acrylate, butyl acrylate, iso-pentyl acrylate, n-hexyl acrylate, 2-ethyl hexyl acrylate, and their (C<sub>1</sub>-C<sub>12</sub>)alkyl methacrylate analogs such as, e.g., methyl methacrylate, ethyl methacrylate, propyl methacrylate, iso-propyl 15 methacrylate, butyl methacrylate, hexyl methacrylate, decyl methacrylate.

The elastomeric phase may, optionally, include up to about 25 percent by weight ("wt%") of one or more monomers selected from (C<sub>2</sub>-C<sub>8</sub>)olefin monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers.

20 As used herein, the term "(C<sub>2</sub>-C<sub>8</sub>)olefin monomers" means a compound having from 2 to 8 carbon atoms per molecule and having a single site of ethylenic unsaturation per molecule. Suitable (C<sub>2</sub>-C<sub>8</sub>)olefin monomers include, e.g., ethylene, propene, 1-butene, 1-pentene, heptene.

25 Suitable vinyl aromatic monomers include, e.g., styrene and substituted styrenes having one or more alkyl, alkoxy, hydroxyl or halo substituent group attached to the aromatic ring, including, e.g.,  $\alpha$ -methyl styrene, p-methyl styrene, vinyl toluene, vinyl xylene, trimethyl styrene, butyl

styrene, chlorostyrene, dichlorostyrene, bromostyrene, p-hydroxystyrene, methoxystyrene and vinyl-substituted condensed aromatic ring structures, such as, e.g., vinyl naphthalene, vinyl anthracene, as well as mixtures of vinyl aromatic monomers.

5 As used herein, the term "monoethylenically unsaturated nitrile monomer" means an acyclic compound that includes a single nitrile group and a single site of ethylenic unsaturation per molecule and includes, e.g., acrylonitrile, methacrylonitrile,  $\alpha$ - chloro acrylonitrile.

The elastomeric phase may, optionally, include a minor amount, e.g., 10 up to 5 wt%, of repeating units derived from a polyethylenically unsaturated "crosslinking" monomer, e.g., butylene diacrylate, divinyl benzene, butene diol dimethacrylate, trimethylolpropane tri(meth)acrylate. As used herein, the term "polyethylenically unsaturated" means having two or more sites of ethylenic unsaturation per molecule.

15 The elastomeric phase may, particularly in those embodiments wherein the elastomeric phase has repeating units derived from alkyl (meth)acrylate monomers, include a minor amount, e.g., up to 5 wt% of repeating units derived from a polyethylenically unsaturated "graftlinking" monomer.

Suitable graftlinking monomers include those monomers having a first site of 20 ethylenic unsaturation with a reactivity similar to that of the monoethylenically unsaturated monomers from which the respective substrate or superstrate is derived and a second site of ethylenic unsaturation with a relative reactivity that is substantially different from that of the monoethylenically unsaturated monomers from which the elastomeric phase 25 is derived so that the first site reacts during synthesis of the elastomeric phase and the second site is available for later reaction under different reaction conditions, e.g., during synthesis of the rigid thermoplastic phase. Suitable

graftlinking monomers include, e.g., allyl methacrylate, diallyl maleate, triallyl cyanurate.

In a preferred embodiment, the elastomeric phase comprises from 60 to 100 wt% repeating units derived from one or more conjugated diene

5 monomers and from 0 to 40 wt% repeating units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers, such as, for example, a styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer or a styrene-butadiene-acrylonitrile copolymer.

10 In an alternative preferred embodiment, the elastomeric phase comprises repeating units derived from one or more (C<sub>1</sub>-C<sub>12</sub>)alkyl acrylate monomers. In a more highly preferred embodiment, the rubbery polymeric substrate comprises from 40 to 95 wt% repeating units derived from one or more (C<sub>1</sub>-C<sub>12</sub>)alkyl acrylate monomers, more preferably from one or more 15 monomers selected from ethyl acrylate, butyl acrylate and n-hexyl acrylate.

In a preferred embodiment, the elastomeric phase is made by aqueous emulsion polymerization in the presence of a free radical initiator, e.g., an azonitrile initiator, an organic peroxide initiator, a persulfate initiator or a redox initiator system, and, optionally, in the presence of a chain transfer 20 agent, e.g., an alkyl mercaptan and coagulated to form particles of elastomeric phase material. In a preferred embodiment, the emulsion polymerized particles of elastomeric phase material have a weight average particle size of 50 to 800 nm, more preferably, of from 100 to 500 nm, as measured by light transmission. The size of emulsion polymerized elastomeric particles may 25 optionally be increased by mechanical or chemical agglomeration of the emulsion polymerized particles, according to known techniques.

(b) Rigid Thermoplastic Phase

The rigid thermoplastic resin phase comprises one or more thermoplastic polymers and exhibits a  $T_g$  of greater than 25°C, preferably greater than or equal to 90°C and even more preferably greater than or equal to 100°C.

5 In a preferred embodiment, the rigid thermoplastic phase comprises a polymer or a mixture of two or more polymers each having repeating units derived from one or more monomers selected from the group consisting of (C<sub>1</sub>-C<sub>12</sub>)alkyl (meth)acrylate monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers. Suitable (C<sub>1</sub>-C<sub>12</sub>)alkyl (meth)acrylate monomers, vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers are those set forth above in the description of the elastomeric phase.

10

In a highly preferred embodiment, rigid thermoplastic phase comprises one or more vinyl aromatic polymers. Suitable vinyl aromatic polymers comprise at least 50 wt% repeating units derived from one or more vinyl aromatic monomers.

15

In a preferred embodiment, the rigid thermoplastic resin phase comprises a vinyl aromatic polymer having first repeating units derived from one or more vinyl aromatic monomers and having second repeating units derived from one or more monoethylenically unsaturated nitrile monomers.

20

The rigid thermoplastic phase is made according to known processes, e.g., mass polymerization, emulsion polymerization, suspension polymerization or combinations thereof, wherein at least a portion of the rigid thermoplastic phase is chemically bonded, i.e., "grafted" to the elastomeric phase via reaction with unsaturated sites present in the elastomeric phase. The unsaturated sites in the elastomeric phase are provided, e.g., by residual unsaturated sites in repeating units derived from a

25

conjugated diene or by residual unsaturated sites in repeating units derived from a graftlinking monomer.

In a preferred embodiment, at least a portion of the rigid thermoplastic phase is made by an aqueous emulsion or aqueous suspension

5 polymerization reaction in the presence of elastomeric phase and a polymerization initiator system, e.g., a thermal or redox initiator system.

In an alternative preferred embodiment, at least a portion of the thermoplastic phase is made by a mass polymerization process, wherein particles of the material from which the elastomeric phase is to be formed are 10 dispersed in a mixture of the monomers from which the rigid thermoplastic phase is to be formed and the monomers of the mixture are then polymerized to form the rubber modified thermoplastic resin.

The amount of grafting that takes place between the rigid thermoplastic phase and the elastomeric phase varies with the relative 15 amount and composition of the elastomeric phase. In a preferred embodiment, from 10 to 90 wt%, preferably from 30 to 80 wt%, even more preferably 65 to 80 wt% of the rigid thermoplastic phase is chemically grafted to the elastomeric phase and from 10 to 90 wt%, preferably from 20 to 70 wt%, more preferably from 20 to 35 wt% of the rigid thermoplastic phase remains 20 "free, i.e., non-grafted.

The rigid thermoplastic phase of the rubber modified thermoplastic resin may be formed: (i) solely by polymerization carried out in the presence of the elastomeric phase or (ii) by addition of one or more separately polymerized rigid thermoplastic polymers to a rigid thermoplastic polymer 25 that has been polymerized in the presence of the elastomeric phase. In a preferred, less than 10 pbw, more preferably less than 5 pbw of separately polymerized rigid thermoplastic polymer is added per 100 pbw of the thermoplastic resin composition of the present invention. Most preferably no

separately polymerized rigid thermoplastic polymer is added to the thermoplastic resin composition of the present invention.

In a preferred embodiment, the rubber modified thermoplastic resin comprises an elastomeric phase comprising a polymer having repeating units derived from one or more conjugated diene monomers, and, optionally, further comprising repeating units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers, and the rigid thermoplastic phase comprises a polymer having repeating units derived from one or more monomers selected from vinyl aromatic monomers and monoethylenically unsaturated nitrile monomers.

5      derived from one or more conjugated diene monomers, and, optionally,  
further comprising repeating units derived from one or more monomers  
selected from vinyl aromatic monomers and monoethylenically unsaturated  
nitrile monomers, and the rigid thermoplastic phase comprises a polymer  
having repeating units derived from one or more monomers selected from  
10     vinyl aromatic monomers and monoethylenically unsaturated nitrile  
monomers.

Each of the polymers of the elastomeric phase and of the rigid thermoplastic resin phase of the rubber modified thermoplastic resin may, provided that the  $T_g$  limitation for the respective phase is satisfied, optionally 15 include up to 10 wt% of third repeating units derived from one or more other copolymerizable monomers such as, e.g., monoethylenically unsaturated carboxylic acids such as, e.g., acrylic acid, methacrylic acid, itaconic acid, hydroxy(C<sub>1</sub>-C<sub>12</sub>)alkyl (meth)acrylate monomers such as, e.g., hydroxyethyl methacrylate; (C<sub>4</sub>-C<sub>12</sub>)cycloalkyl (meth)acrylate monomers such as e.g., 20 cyclohexyl methacrylate; (meth)acrylamide monomers such as e.g., acrylamide and methacrylamide; maleimide monomers such as, e.g., N-alkyl maleimides, N-aryl maleimides, maleic anhydride, vinyl esters such as, e.g., vinyl acetate and vinyl propionate. As used herein, the term "(C<sub>4</sub>-C<sub>12</sub>)cycloalkyl" means a cyclic alkyl substituent group having from 4 to 12 25 carbon atoms per group and the term "(meth)acrylamide" refers collectively to acrylamides and methacrylamides.

Fluoropolymer Additive

Suitable fluoropolymers and methods for making such fluoropolymers are known, see, e.g., U.S Patent Nos. 3,671,487, 3,723,373 and 3,383,092.

Suitable fluoropolymers include homopolymers and copolymers that

- 5 comprise repeating units derived from one or more fluorinated olefin monomers. The term "fluorinated olefin monomer" means an olefin monomer that includes at least one fluorine atom substituent. Suitable fluorinated olefin monomers include, e.g., fluoroethylenes such as, e.g.,  $\text{CF}_2=\text{CF}_2$ ,  $\text{CHF}=\text{CF}_2$ ,  $\text{CH}_2=\text{CF}_2$ ,  $\text{CH}_2=\text{CHF}$ ,  $\text{CClF}=\text{CF}_2$ ,  $\text{CCl}_2=\text{CF}_2$ ,  $\text{CClF}=\text{CClF}$ ,
- 10  $\text{CHF}=\text{CCl}_2$ ,  $\text{CH}_2=\text{CClF}$ , and  $\text{CCl}_2=\text{CClF}$  and fluoropropylenes such as, e.g.,  $\text{CF}_3\text{CF}=\text{CF}_2$ ,  $\text{CF}_3\text{CF}=\text{CHF}$ ,  $\text{CF}_3\text{CH}=\text{CF}_2$ ,  $\text{CF}_3\text{CH}=\text{CH}_2$ ,  $\text{CF}_3\text{CF}=\text{CHF}$ ,  $\text{CHF}_2\text{CH}=\text{CHF}$  and  $\text{CF}_3\text{CH}=\text{CH}_2$ . In a preferred embodiment, the fluorinated olefin monomer is one or more of tetrafluoroethylene ( $\text{CF}_2=\text{CF}_2$ ), chlorotrichloroethylene ( $\text{CClF}=\text{CF}_2$ ), vinylidene fluoride ( $\text{CH}_2=\text{CF}_2$ ) and
- 15 hexafluoropropylene ( $\text{CF}_2=\text{CFCF}_3$ ).

Suitable fluorinated olefin homopolymers include e.g., poly(tetra-fluoroethylene), poly(hexafluoroethylene).

Suitable fluorinated olefin copolymers include copolymers comprising repeating units derived from two or more fluorinated olefin copolymers such

- 20 as, e.g., poly(tetrafluoroethylene-hexafluoroethylene), and copolymers comprising repeating units derived from one or more fluorinated monomers and one or more non-fluorinated monoethylenically unsaturated monomers that are copolymerizable with the fluorinated monomers such as, e.g., poly(tetrafluoroethylene-ethylene-propylene) copolymers. Suitable non-
- 25 fluorinated monoethylenically unsaturated monomers include e.g., olefin monomers such as, e.g., ethylene, propylene, butene, acrylate monomers such as e.g., methyl methacrylate, butyl acrylate, vinyl ethers, such as, e.g.,

cyclohexyl vinyl ether, ethyl vinyl ether, n-butyl vinyl ether, vinyl esters such as, e.g., vinyl acetate, vinyl versatate.

In a highly preferred embodiment, the fluoropolymer is a poly(tetrafluoroethylene) homopolymer ("PTFE").

5 In a preferred embodiment, a fluoropolymer is added to the rubber modified thermoplastic resin in the form of a fluoropolymer additive that comprises particles of fluoropolymer encapsulated in a second polymer.

10 In a preferred embodiment, the fluoropolymer additive comprises from 30 to 70 wt%, more preferably 40 to 60 wt%, of the fluoropolymer and from 30 to 70 wt%, more preferably 40 to 60 wt%, of the second polymer.

The fluoropolymer additive is made by combining a fluoropolymer, in the form of an aqueous dispersion of fluoropolymer particles, with a second polymer, precipitating the combined fluoropolymer particles and second polymer and then drying the precipitate to form the fluoropolymer additive.

15 In a preferred embodiment, the fluoropolymer particles range in size from 50 to 500 nanometers ("nm"), as measured by electron microscopy.

20 In a preferred embodiment, the fluoropolymer additive is made by emulsion polymerization of one or more monoethylenically unsaturated monomers in the presence of the aqueous fluoropolymer dispersion of the present invention to form a second polymer in the presence of the fluoropolymer. Suitable monoethylenically unsaturated monomers are disclosed above. The emulsion is then precipitated, e.g., by addition of sulfuric acid. The precipitate is dewatered, e.g., by centrifugation, and then dried to form a fluoropolymer additive that comprises fluoropolymer and an associated second polymer. The dry emulsion polymerized fluoropolymer additive is in the form of a free-flowing powder.

25 In a preferred embodiment, the monoethylenically unsaturated monomers that are emulsion polymerized to form the second polymer

comprise one or more monomers selected from vinyl aromatic monomers, monoethylenically unsaturated nitrile monomer and (C<sub>1</sub>-C<sub>12</sub>)alkyl (meth)acrylate monomers.

In a highly preferred embodiment, the second polymer comprises

5 repeating units derived from styrene and acrylonitrile. More preferably, the second polymer comprises from 60 to 90 wt% repeating units derived from styrene and from 10 to 40 wt% repeating units derived from acrylonitrile.

The emulsion polymerization reaction mixture may optionally include emulsified or dispersed particles of a third polymer, such as, e.g., an

10 emulsified butadiene rubber latex.

The emulsion polymerization reaction is initiated using a conventional free radical initiator such as, e.g., an organic peroxide compound, such as e.g., benzoyl peroxide, a persulfate compound, such as, e.g., potassium persulfate, an azonitrile compound such as e.g., 2,2'-azobis-2,3,3-trimethylbutyronitrile,

15 or a redox initiator system, such as, e.g., a combination of cumene hydroperoxide, ferrous sulfate, tetrasodium pyrophosphate and a reducing sugar or sodium formaldehyde sulfoxylate.

A chain transfer agent such as, e.g., a (C<sub>9</sub>-C<sub>13</sub>) alkyl mercaptan compound such as nonyl mercaptan, t-dodecyl mercaptan, may, optionally, 20 be added to the reaction vessel during the polymerization reaction to reduce the molecular weight of the second polymer. In a preferred embodiment, no chain transfer agent is used.

In a preferred embodiment, the stabilized fluoropolymer dispersion is charged to a reaction vessel and heated with stirring. The initiator system 25 and the one or more monoethylenically unsaturated monomers are then charged to the reaction vessel and heated to polymerize the monomers in the presence of the fluoropolymer particles of the dispersion to thereby form the second polymer.

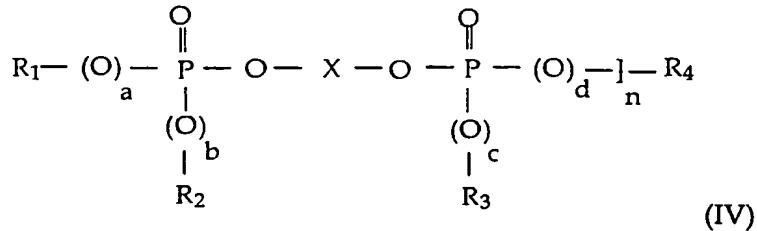
Suitable fluoropolymer additives and emulsion polymerization methods are disclosed in EP 0 739 914 A1.

In a preferred embodiment, the second polymer exhibits a weight average molecular weight ("M<sub>w</sub>") of from  $75 \times 10^3$  to  $800 \times 10^3$ , a number average molecular weight ("M<sub>n</sub>") of from  $30 \times 10^3$  to  $200 \times 10^3$  and a polydispersity (M<sub>w</sub>/M<sub>n</sub>) of less than or equal to 6.

Phosphorus-containing Flame Retardant Compound

Phosphorus-containing compounds suitable as the phosphorus-containing flame retardant compound of the present invention are known compounds including monophosphate esters such as, for example, triphenyl phosphate, tricresyl phosphate, tritolyl phosphate, diphenyl tricresylphosphate, phenyl bisdodecyl phosphate, ethyl diphenyl phosphate, as well as diphosphate esters and oligomeric phosphates such as, for example, resorcinol diphosphate, diphenyl hydrogen phosphate, bisphenol A diphosphate, 2-ethylhexyl hydrogen phosphate. Suitable oligomeric phosphate compounds are set forth in coassigned U.S. Patent Number 5,672,645, to Johannes C. Gossens et al for a "Polymer Mixture Having Aromatic Polycarbonate, Styrene Containing Copolymer and/or Graft Copolymer and a Flame Retardant, Articles Formed Therefrom", the disclosure of which is hereby incorporated herein by reference.

In a preferred embodiment, the phosphorus-containing compound of the present invention is an oligomer compound according to the structural formula (IV):



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are each independently aryl, which may be optionally substituted with halo or alkyl,

$\text{X}$  is arylene, optionally substituted with halo or alkyl,

5 a, b, c and d are each independently 0 or 1, and

$\text{n}$  is an integer of from 1 to 5.

As used herein, aryl means a monovalent radical containing one or more aromatic rings per radical, which may optionally be substituted on the one or more aromatic rings with one or more alkyl groups, each preferably

10  $(\text{C}_1\text{-C}_6)$ alkyl and which, in the case wherein the radical contains two or more rings, may be fused rings.

As used herein, arylene means a divalent radical containing one or more aromatic rings per radical, which may optionally be substituted on the one or more aromatic rings with one or more alkyl groups, each preferably

15  $(\text{C}_1\text{-C}_6)$ alkyl and which, in the case wherein the divalent radical contains two or more rings, the rings may be fused or may be joined by a non-aromatic linkages, such as for example, an alkylene, alkylidene, any of which may be substituted at one or more sites on the aromatic ring with a halo group or  $(\text{C}_1\text{-C}_6)$ alkyl group.

20 In a preferred embodiment,  $\text{X}$  is a residue derived from resorcinol or hydroquinone.

In a preferred embodiment,  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  are each phenyl, a, b, c and d are each 1,  $\text{X}$  is phenylene and  $\text{n}$  is 2 or wherein the phosphate containing compound is a blend of phosphorus containing oligomers with  $\text{n}$

25 having an average value of from 1 to 2, more preferably from 1.2 to 1.7.

Other Additives

The thermoplastic resin composition of the present invention may optionally also contain various conventional additives, such as:

(1) antioxidants, such as, e.g., organophosphites, e.g., tris(nonylphenyl)phosphite, (2,4,6-tri-tert-butylphenyl)(2-butyl-2-ethyl-1,3-propanediol)phosphite, bis(2,4-di-t-butylphenyl)pentaerythritol diphosphite or distearyl pentaerythritol diphosphite, as well as alkylated monophenols, polyphenols, alkylated reaction products of polyphenols with dienes, such as, e.g., butylated reaction products of para-cresol and dicyclopentadiene, alkylated hydroquinones, hydroxylated thiadiphenyl ethers, alkylidene-bisphenols, benzyl compounds, acylaminophenols, esters of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, esters of beta-(5-tert-butyl-4-hydroxy-3-methylphenyl) propionic acid with mono- or polyhydric alcohols, esters of thioalkyl or thioaryl compounds, such as, e.g., distearylthiopropionate, dilaurylthiopropionate, ditridecylthiodipropionate, amides of beta-(3,5-di-tert-butyl-4-hydroxyphenol)-propionic acid;

(2) UV absorbers and light stabilizers such as, e.g., (i) 2-(2'-hydroxyphenyl)-benzotriazoles, 2-Hydroxy-benzophenones; (ii) esters of substituted and unsubstituted benzoic acids, (iii) acrylates, (iv) nickel compounds;

(3) metal deactivators, such as, e.g., N,N'-diphenyloxalic acid diamide, 3-salicyloylamino-1,2,4-triazole;

(4) peroxide scavengers, such as, e.g., (C<sub>10</sub>-C<sub>20</sub>)alkyl esters of  $\beta$ -thiodipropionic acid, mercapto benzimidazole;

- (5) polyamide stabilizers;
- (6) basic co-stabilizers, such as, e.g., melamine, polyvinylpyrrolidone, triallyl cyanurate; urea derivatives, hydrazine derivatives; amines, polyamides, polyurethanes;
- 5 (7) sterically hindered amines such as, e.g., triisopropanol amine or the reaction product of 2,4-dichloro-6-(4-morpholinyl)-1,3,5-triazine with a polymer of 1,6-diamine, N,N'-Bis(-2,2,4,6-tetramethyl-4-piperidenyl) hexane;
- 10 (8) neutralizers such as magnesium stearate, magnesium oxide, zinc oxide, zinc stearate, hydrotalcite;
- (9) fillers and reinforcing agents, such as, e.g., silicates, TiO<sub>2</sub>, glass fibers, carbon black, graphite, calcium carbonate, talc, mica;
- (9) other additives such as, e.g., lubricants such as, e.g., pentaerythritol tetrastearate, EBS wax, silicone fluids, plasticizers, optical brighteners,
- 15 pigments, dyes, colorants, flameproofing agents; anti-static agents; blowing agents;
- (10) other flame retardant additives such as, for example, borate flame retardant compounds, in addition to the above described phosphorus-containing flame retardant additive.

20 The thermoplastic resin composition of the present invention is made by combining and mixing the components of the composition of the present invention under conditions suitable for the formation of a blend of the components, such as for example, by melt mixing using, for example, a two-roll mill, a Banbury mixer or a single screw or twin-screw extruder, and,

25 optionally, then reducing the composition so formed to particulate form, e.g., by pelletizing or grinding the composition.

The thermoplastic resin composition of the present invention can be molded into useful shaped articles by a variety of means such as injection molding, extrusion, rotational molding, blow molding and thermoforming to form articles such as, for example, computer and business machine housings, 5 home appliances.

Examples 1-2 and Comparative Examples C1-C3

The components used in the thermoplastic resin compositions of Examples 1-2 of the present invention and of Comparative Examples C1-C3 were as follows:

10 PC-1 Branched polycarbonate resin derived from bisphenol A, phosgene and having a weight average molecular weight of about 32,000 g/mol.

PC-2: Linear polycarbonate resin derived from bisphenol A, phosgene and trimellitic trichlorite and having a weight average

15 ABS: molecular weight of about 31,000 g/mol.

Emulsion polymerized acrylonitrile-butadiene-styrene ("ABS") graft copolymer comprising 50 pbw of a discontinuous elastomeric phase (butadiene) and 50 pbw of a rigid thermoplastic phase (copolymer of 75 pbw styrene and 25 pbw acrylonitrile);

20 TSAN: Additive made by copolymerizing styrene and acrylonitrile in the presence of an aqueous dispersion of PTFE (50 wt% PTFE, 50wt% styrene-acrylonitrile copolymer).

RDP Resorcinol diphosphate (Rheofos RDP, from FMC Corporation, 25 Ltd.).

TiO<sup>2</sup> Titanium dioxide (RFC 5, Tioxide Europe).

The respective compositions were made by combining the above-listed components in the relative amounts (in pbw) set forth in TABLE I in a twin

screw extruder. The compositions were then injection molded at 255°C into a 60°C mold to form samples for testing.

The samples were tested according to the following methods: melt volume rate was measured according to ISO 1133 at 260°C using a 5 kilogram weight, notched impact Izod performance was measured according to ISO 180, Vicat B temperature was measured according to ISO 306 tensile properties were measured according to ISO 527, flame retardant properties were measured according to UL 94 and CSTBNF P92 505. The compositions were evaluated for compliance with DIN/VDE 0472, Part 815, Test B which requires a fluorine content of less than or equal to 0.1 wt%.

Results of the testing are set forth in TABLES I for each of the compositions of Examples 1-2 and Comparative Examples C1-C3 and as melt viscosity ("MVR") expressed in milliliters per 10 minute ("ml/10 min"), notched Izod impact strength at room temperature ("RT"), 10°C and 0°C expressed in kiloJoules per square meter ("KJ/m<sup>2</sup>"), tensile strength and tensile modulus in Newtons per square millimeter ("N/mm<sup>2</sup>"), elongation at break as percent of original length (%), Vicat B temperature expressed in °C, UL 94 classification as V-0, V-1 or V-2, total flame out time in seconds ("s"), number of flaming drips per 5 samples, and compliance with DIN/VDE 0472 Part 815, Test B and CSTBNF P92 505, expressed as a rating of "Pass" or "Fail".

The results of the testing are set forth below in TABLE I for each of the compositions of Examples 1-2 and Comparative Examples C1-C3.

TABLE I

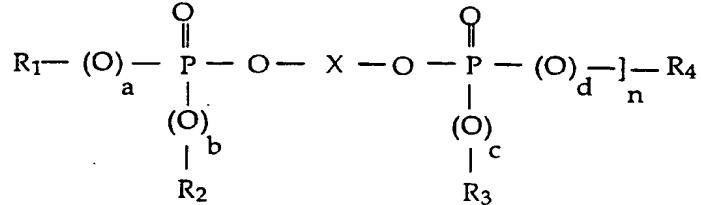
	C1	C2	C3	1	2
PC-1	84.25	84.15	83.95	84.05	--
PC-2	--	--	--	--	84.05
ABS	6	6	6	6	6
RDP	9	9	9	9	9
TSAN	—	0.1	0.3	0.2	0.2
Additives	0.4	0.4	0.4	0.4	0.4
TiO <sub>2</sub>	0.35	0.35	0.35	0.35	0.35
<u>Performance</u>					
MVR at 260°C (ml/10 min)	9.8	9.2	8.1	8.4	16.7
Notched Izod Impact (KJ/m <sup>2</sup> )					
RT	43.9	43.9	46.4	44.0	52.3
10°	17.6	18.4	18.8	17.9	45.5
0°	16.2	16.6	16.8	16.3	19.1
Tensile Modulus (N/mm <sup>2</sup> )	2611	2579	2631	2590	2640
Tensile Strength at yield (N/mm <sup>2</sup> )	64.9	64.5	64.4	64.6	64.0
Elongation at break (%)	46	72	66	74	107
Vicat B (°C)	111.4	112.4	112.6	112.8	111.4
UL 94	V-2	V-1	V-0	V-0	V-0
Flame out time (s)	98	81	14	23	13
Flaming drips	5	0	0	0	0
DIN/VDE 0472, Part 815, Test B	Pass	Pass	Fail	Pass	Pass
NF P92 505	Fail	Fail	Pass	Pass	Pass

The composition of the present invention meets the low fluorine content requirements of DIN/VDE 0472 Part 815, Test B, yet unexpectedly provides high performance and good flame retardant properties.

## CLAIMS

1. A thermoplastic resin composition, comprising:
  - (a) an aromatic polycarbonate resin,
  - (b) a rubber modified graft copolymer comprising a discontinuous elastomeric phase dispersed in a continuous rigid thermoplastic phase, wherein at least a portion of the rigid thermoplastic phase is chemically grafted to the elastomeric phase,
  - (c) a phosphorus containing flame retardant compound, and
  - (d) a fluoropolymer, in an amount effective improve the flame retardant performance of the composition, provided that the fluorine content of the composition does not exceed 0.1 percent by weight fluorine.
2. The composition of claim 1, wherein the composition comprises from 60 to 95 parts by weight of the polycarbonate resin, from 1 to 15 parts by weight of the rubber modified graft copolymer, from 3 to 15 parts by weight of the phosphorus containing flame retardant compound and wherein the amount of fluoropolymer is effective to provide a fluorine content of from 0.038 to 0.1 parts by weight of the fluoropolymer, each based on 100 pbw of the composition
3. The composition of claim 1, wherein the aromatic polycarbonate resin comprises a linear aromatic polycarbonate resin.
4. The composition of claim 1, wherein the aromatic polycarbonate resin comprises a branched aromatic polycarbonate resin.
5. The composition of claim 1, wherein the elastomeric phase comprises a polybutadiene rubber or a poly(styrene-butadiene) rubber and the rigid thermoplastic phase comprises structural units derived from one or more monomers selected from vinyl aromatic monomers and a monoethylenically unsaturated nitrile monomers.

6. The composition of claim 5, wherein rigid phase comprises a copolymer of derived from monomers selected from the group consisting of styrene,  $\alpha$ -methyl styrene and acrylonitrile.
7. The composition of claim 1, wherein the phosphorus containing compound comprises a compound according to the structural formula:



wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each independently aryl, which may be optionally substituted with halo or alkyl,  
X is arylene, optionally substituted with halo or alkyl,  
a, b, c and d are each independently 0 or 1, and  
n is an integer of from 1 to 5.

8. The composition of claim 7, wherein, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are each phenyl, a, b, c and d are each 1, X is phenylene.
9. The composition of claim 7, wherein n is 2
10. The composition of claim 7, wherein the phosphate containing compound is a blend of phosphorus containing oligomers with n having an average value of from 1 to 2.
11. The composition of claim 1, wherein the fluoropolymer is a tetrafluoroethylene polymer.

12. The composition of claim 1, wherein the fluoropolymer is added to the composition in the form of an additive made by emulsion polymerization of one or more monoethylenically unsaturated monomers in the presence of an aqueous dispersion of the fluoropolymer to form a second polymer in the presence of the fluoropolymer.
13. The composition of claim 12, wherein the additive is made by emulsion polymerization of styrene and acrylonitrile in the presence of an aqueous dispersion of the fluoropolymer.
14. An article molded from the composition of claim 1.

# INTERNATIONAL SEARCH REPORT

	National Application No PCT/US 99/07727
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**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08L69/00 C08K5/51 // (C08L69/00, 51:04, 27:18)

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 594 021 A (BAYER AG) 27 April 1994 (1994-04-27) page 3, line 11 - page 4, line 26; claims 1,10 page 8, line 44-46 page 8, line 54 - page 9, line 1 ----	1-14
X	EP 0 714 932 A (CHEIL IND INC) 5 June 1996 (1996-06-05) claims 1,2,4 ----	1-3,5-11
X	EP 0 700 968 A (CHEIL IND INC) 13 March 1996 (1996-03-13) claims 1,4 ----	1-3,5-11 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 July 1999	04/08/1999
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl Fax: (+31-70) 340-3016	Voigtländer, R

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/07727

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 640 655 A (BAYER AG) 1 March 1995 (1995-03-01) page 5, line 45-48 page 11, line 8-10 page 11, line 19-34; claims 1,10 ----	1-14
X	EP 0 693 495 A (BAYER AG) 24 January 1996 (1996-01-24) page 6, line 46-49 page 8, line 4,5 page 9, line 35-46; claims 5,7,8 ----	1-6, 11-14
A	EP 0 700 969 A (CHEIL IND INC) 13 March 1996 (1996-03-13) page 4, line 29,30; claims 1,2 ----	1
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Information on patent family members

International Application No  
PCT/US 99/07727

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